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14. ABSTRACT Improved quantum (TD-DFT with explicit consideration of reaction fields) and statistical mechanical (pseudo-atomistic Monte Carlo/Molecular Dynamics) methods have been used to guide the design of novel new organic electroactive materials (e.g., electro-optic binary chromophore organic glasses). These new materials have yielded electro-optic coefficients as high as 450 pm/V (15 times lithium niobate) with auxiliary properties of modest optical loss (< 2 dB/cm) and good thermal stability (material glass transition temperatures > 200°C). First principles simulation of electro-optic activity has been achieved for the first time and theoretical conclusions have been verified by a number of new measurement techniques including femtosecond, wavelength-agile hyper Rayleigh scattering (HRS), attenuated total reflection (ATR) using a rutile prism for measurements at 1.3 and 1.55 microns wavelength, polarized absorption spectroscopy, and molecular level resolution techniques.					
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REALIZATION OF NEW AND ENHANCED MATERIALS PROPERTIES THROUGH NANOSTRUCTURAL CONTROL

Larry R. Dalton and Bruce H. Robinson, Departments of Chemistry & Electrical Engineering,
University of Washington, Seattle, WA 98195-1700

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Photonic/electronic integration to achieve dramatic SWaP (size, weight, and power) and specific performance improvements (e.g., Gain in RF photonic applications, bandwidth, detector sensitivity, etc.) is seen as increasingly important for emerging defense systems. Organic materials are among the most promising candidates for such integration; however, their utilization is well-recognized to depend on improvement of specific properties (e.g., optical nonlinearity, photostability, etc.). With support from AFOSR (FA9550-06-1-0042), we have achieved dramatic improvements (exceeding a Moore's Law rate) in the optical nonlinearity and auxiliary properties of organic polymeric and dendritic materials. This has been accomplished through use of an integrated Real-Time, Time-Dependent Density Functional Theory (RTTDDFT) and Pseudo-Atomistic Monte Carlo/Molecular Dynamics (PAMCMD) approach to gain a quantitative understanding of molecular and macroscopic optical nonlinearity, molecular organization defining lattice symmetry (order parameters), reaction fields (dielectric permittivity and index of refraction properties), and physical properties such as density and material glass transition temperatures. Theory-guided nano-engineering of polymer and dendrimer materials has led to new classes of materials (e.g., Binary Chromophore Organic Glasses, BCOGs) exhibiting dramatic improvements in electro-optic activity, optical transparency, photostability, and thermal stability and has facilitated the introduction of new device concepts (e.g., integration of organic nonlinear optical materials into nano-slot silicon photonic waveguides). Hallmark achievements include realization of electro-optic activity of greater than 300 pm/V in thin films (exhibiting good stability and low optical loss) and approaching 200 pm/V in devices; production of all-organic and organic/silicon photonic electro-optic devices exhibiting drive (V_{π}) voltages on the order of 0.25 V; observation of optical rectification (photodetection) with micro-to-milliwatt optical powers; and demonstration of all-optical signal processing to 5 THz using micro-to-milliwatt optical control powers. Beyond specific device related improvements, the broad understanding of the intra and intermolecular interactions that define the physical properties of polymer and dendrimer materials has been advanced. In addition to theoretical advances, new diagnostic technologies are being developed that permit direct measurement of electrostatic interactions among components of multi-components materials (composites, multi-dendrimer/polymer supra/supramolecular materials). The broader understanding of electroactive polymer and dendrimer materials is relevant to the nano-engineering of improved organic light emitting device, electronic, photovoltaic, and photorefractive materials and to optimizing not only polarizability and hyperpolarizability (nonlinear optical properties) but also to optimizing charge transport and injection (extraction) relevant to electronic performance.

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Annual accomplishments (200 words max): Improved quantum (TD-DFT with explicit consideration of reaction fields) and statistical mechanical (pseudo-atomistic Monte Carlo/Molecular Dynamics) methods have been used to guide the design of novel new organic electroactive materials (e.g., electro-optic binary chromophore organic glasses). These new materials have yielded electro-optic coefficients as high as 450 pm/V (15 times lithium niobate) with auxiliary properties of modest optical loss (< 2 dB/cm) and good thermal stability (material glass transition temperatures $> 200^{\circ}\text{C}$). First principles simulation of electro-optic activity has been achieved for the first time and theoretical conclusions have been verified by a number of new measurement techniques including femtosecond, wavelength-agile hyper Rayleigh scattering (HRS), attenuated total reflection (ATR) using a rutile prism for measurements at 1.3 and 1.55 microns wavelength, polarized absorption spectroscopy, and molecular level resolution techniques. The paradigm of using custom-designed intermolecular electrostatic interactions to enhance the acentric order of dipolar chromophores has also been verified by applying laser-assisted poling techniques to binary chromophore organic glasses containing azobenzene chromophores.

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